

TRACE METAL ANALYSIS OF ROCKS AND SEDIMENTS BY GRAPHITE
FURNACE ATOMIC ABSORPTION SPECTROSCOPY

By Arthur J. Horowitz

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ABSTRACT

An accurate and precise method for the determination of seven common trace metals (Cd, Co, Cr, Cu, Ni, Pb, and Zn) in rocks and sediments, from as little as 5 milligrams of sample, is presented. The method employs a wet digestion in Teflon¹ beakers using a combination of HF, HClO₄, and HNO₃. Quantitation is carried out by graphite furnace atomic absorption spectrophotometry using mixed salt standards, and where appropriate, deuterium source background correction, or matrix modifiers, or both. Comparison of data generated by this procedure, with published data for U.S. Geological Survey Standard Rocks and National Bureau of Standards sediments, as well as through inter- and intralaboratory comparisons on natural sediment samples, indicate that precise and accurate results can be obtained.

¹The use of brand names in this report is for identification purposes only, and does not constitute an endorsement by the U.S. Geological Survey.

INTRODUCTION

The chemical analysis of rocks and sediments is performed for a variety of environmental and petrological purposes. For example, chemical data are used to identify various rock types. Also, stream-bottom sediments contain significantly higher concentrations of many metals than are found in the overlying water. As such, they can be analyzed for pollutant contributions to the environment. Of particular interest to aquatic chemists and geochemists are the metal levels associated with suspended sediment. Suspended sediment is important for several reasons: (1) as with bed material, it contains significantly higher metal levels than found in the dissolved state, (2) it is the medium on or in which the majority of metals are transported in aquatic systems, and (3) it can be in intimate contact with or is ingested by many aquatic organisms.

The chemical analysis of suspended sediment can be a problem because in many aquatic systems its concentration can be low (<5 mg/L); thus, the material available may be too limited for flame atomic absorption techniques. The investigator is left with two choices: collect and process large volumes of water to obtain sufficient suspended sediment so that flame atomic absorption techniques can be employed, or use a more sensitive analytical method capable of quantitating metals in very small (~ 5 mg) samples. The latter approach is preferred for several reasons such as less field sampling time, less labor intensity, and less chance of sample contamination.

A wet digestion employing a combination of HF, HClO₄, and HNO₃ acids is used to solubilize the sample to determine various metal concentrations in small quantities of solid material. Quantitation is achieved by graphite furnace atomic absorption spectroscopy. Where appropriate, deuterium source background correction and/or matrix modifiers are used in conjunction with pyrolytically coated graphite tubes. This method does not require the use of a platform. The upper and lower concentration limits of the metals analyzed by this technique are outlined in table 1. Samples that contain analyte concentrations greater than the upper limit may be analyzed after appropriate dilution or by flame atomic absorption spectroscopy (Horowitz and Elrick, 1985). Samples containing analyte concentrations less than the lower limit may be analyzed by carrying out multiple sample injections and drying steps, prior to ashing (charring) and atomization.

The author wishes to express his appreciation to Douglas Shrader, Deen Johnson, and Fred Delles of the Varian Instrument Company for their advice during the methods development stage of this study.

Table 1.-Upper and lower limits of the method
for various constituents

Constituent	Lower Limit ¹		Upper Limit	
	Sample (mg/kg)	Solution (µg/L)	Sample (mg/kg)	Solution (µg/L)
Cadmium	0.15	0.015	20	2
Cobalt	2	.2	600	60
Chromium	3	.3	400	40
Copper	2	.2	400	40
Lead	3	.3	250	25
Nickel	2	.2	600	60
Zinc	2	.2	160	16

¹Value refers to a single injection; lower limits can be achieved through the use of multiple injections prior to charring and atomization.

SUMMARY

Sediment or rock samples are dried, ground, and homogenized. An aliquot is digested with a combination of HF, HClO₄, and HNO₃, in Teflon beakers, and heated on a hot plate at 200°C. The resulting salts are dissolved in HNO₃ and demineralized water. The solutions are analyzed by graphite furnace atomic absorption spectroscopy using mixed salt standards, and after the addition (in certain cases) of appropriate matrix modifiers, to permit increased ashing temperatures. Interelement interferences, both positive and negative, are removed or compensated for. Further information about the principles of the method can be found in Cruz and van Loon (1974), Johnson and Maxwell (1981), Pinta (1982), and van Loon (1985).

Interferences

Numerous interelement interferences, both positive and negative, exist for graphite furnace atomic absorption spectroscopy for various trace metals and have been documented in Cruz and van Loon (1974), Johnson and Maxwell (1981), Pinta (1982), and van Loon (1985). Interferences are eliminated or compensated for through the removal of silica by the digestion procedure, dilution, the use of mixed salt standards, the use of deuterium source background correction (where applicable and appropriate), the choice of appropriate ashing and atomization temperatures and times, and the use of matrix modifiers (where applicable).

Apparatus

A Varian Model AA-1475 double beam atomic absorption spectrophotometer with microprocessor control and digital display, used with a Varian Model GTA-95 graphite furnace system, and a PSD-95 programmable sample dispenser were used in this study. Instrumental parameters are listed in table 2 and the furnace and autosampler programs are provided in table 3.

Pyrolytically coated graphite furnace tubes.

Teflon beakers, 100 mL capacity, thick wall, capable of withstanding temperatures of 260°C.

Hot plate, electric or gas, capable of at least 250°C.

Perchloric acid hood, with appropriate washdown facility, and gas or electric outlets for the hot plate.

Table 2.--Instrument settings used for the method

Parameters	Cu	Zn	Cd	Pb	Cr	Ni	Co
Wave length (nm)	324.8	213.9	228.8	217.0	357.9	232.0	240.7
Slit (nm)	.5	1	.5	1	.2	.2	⁴ .5
Lamp current (ma)	4	5	4	5	7	4	7
Beam ¹	D	D	D	D	D	S	S
Measurement ²	H	H	H	H	H	A	A
Background corr.	Off	On	On	On	Off	On	On
Modifier	No	Yes ³	Yes ³	Yes ³	No	No	No

¹Beam: single beam (S) or double beam (D).

²Measurement: peak height (H) or peak area (A).

³Modifier: 0.5% H₃PO₄.

⁴Slit for Co: tune on 0.2 μm, then switch to 0.5 μm, do not retune.

Table 3. --Analytical programs for various furnace procedures

Cu

STEP NO.	TEMPERATURE °C.	TIME SEC.	GAS FLOW	GAS TYPE	READ COMMAND
1	75	5.0	3.0	NORMAL	
2	90	4.0	3.0	NORMAL	
3	120	10	3.0	NORMAL	
4	120	5.0	3.0	NORMAL	
5	600	4	3.0	NORMAL	
6	600	10	3.0	NORMAL	
7	600	2.0	0	NORMAL	
8	2300	1.1	0	NORMAL	*
9	2300	2.0	0	NORMAL	*
10	2300	1.0	3.0	NORMAL	*
11	40	10	3.0	NORMAL	
12	40	0	3.0	NORMAL	

SAMPLES AND STANDARDS	TYPE	VOLUME	MODIFIER
BLANK	--	20	
STD 1	46	20	
STD 2	47	20	
STD 3	48	20	
STD 4			
STD 5			
SAMPLES	--	20	

LAST SAMPLE NO. = 45 MULTIPLE INJECTIONS = 1
 NO. OF REPLICATES = 3 LAST DRY PHASE STEP = 2
 RESLOPE RATE = 5 INJECTION TEMP. =AMB
 FIRST SAMPLE NO. = 1

2h

STEP NO.	TEMPERATURE °C.	TIME SEC.	GAS FLOW	GAS TYPE	READ COMMAND
1	75	5.0	3.0	NORMAL	
2	90	30	3.0	NORMAL	
3	120	10	3.0	NORMAL	
4	120	5.0	3.0	NORMAL	
5	600	3.3	3.0	NORMAL	
6	600	20	3.0	NORMAL	
7	600	2.0	0	NORMAL	
8	1900	1.4	0	NORMAL	*
9	1900	2.0	0	NORMAL	*
10	1900	1.0	3.0	NORMAL	*
11	2400	3	3.0	NORMAL	
12	40	11	3.0	NORMAL	

SAMPLES AND STANDARDS	TYPE	VOLUME	MODIFIER
BLANK	--	3	4
STD 1	46	3	4
STD 2	47	3	4
STD 3	48	3	4
STD 4			
STD 5			
SAMPLES	--	3	4

LAST SAMPLE NO. = 45 MULTIPLE INJECTIONS = 1
 NO. OF REPLICATES = 3 LAST DRY PHASE STEP = 2
 RESLOPE RATE = 5 INJECTION TEMP. =AMB
 FIRST SAMPLE NO. = 1

- 1 Maintain gas flow to reduce sensitivity
- 2 'Kicker' step to reduce carryover
- 3 Added volume to spread sample more evenly in the furnace tube

Cd

STEP NO.	TEMPERATURE °C.	TIME SEC.	GAS FLOW	GAS TYPE	READ COMMAND
1	75	5.0	3.0	NORMAL	
2	90	80	3.0	NORMAL	
3	120	10	3.0	NORMAL	
4	120	5.0	3.0	NORMAL	
5	700	3	3.0	NORMAL	
6	700	20	3.0	NORMAL	
7	700	2.0	0	NORMAL	
8	1800	1.5	0	NORMAL	*
9	1800	2.0	0	NORMAL	*
10	1800	1.0	3.0	NORMAL	*
11	2300	3	3.0	NORMAL	
12	40	10	3.0	NORMAL	

SAMPLES AND STANDARDS	TYPE	VOLUME	MODIFIER
BLANK	--	25	15
STD 1	46	25	15
STD 2	47	25	15
STD 3	48	25	15
STD 4			
STD 5			
SAMPLES	--	25	15

LAST SAMPLE NO. = 45 MULTIPLE INJECTIONS = 1
 NO. OF REPLICATES = 3 LAST DRY PHASE STEP = 2
 RESLOPE RATE = 5 INJECTION TEMP. =AMB
 FIRST SAMPLE NO. = 1

4 'Kicker' step to reduce carryover

pb

SAMPLES AND STANDARDS	TYPE	VOLUME	MODIFIER
BLANK	--	20	5
STD 1	46	5	5
STD 2	47	5	5
STD 3	48	5	5
STD 4			
STD 5			
SAMPLES	--	20	5

LAST SAMPLE NO. = 45 MULTIPLE INJECTIONS = 1
 NO. OF REPLICATES = 3 LAST DRY PHASE STEP = 2
 RESLOPE RATE = 5 INJECTION TEMP. =AMB
 FIRST SAMPLE NO. = 1

Cr

STEP NO.	TEMPERATURE °C.	TIME SEC.	GAS FLOW	GAS TYPE	READ COMMAND
1	75	5.0	3.0	NORMAL	
2	90	30	3.0	NORMAL	
3	120	10	3.0	NORMAL	
4	120	5.0	3.0	NORMAL	
5	1000	5	3.0	NORMAL	
6	1000	10	3.0	NORMAL	
7	1000	2.0	0	NORMAL	
8	2600	0.8	0	NORMAL	*
9	2600	2.0	0	NORMAL	*
10	2600	1.0	3.0	NORMAL	*
11	40	12	3.0	NORMAL	

SAMPLES AND STANDARDS	TYPE	VOLUME	MODIFIER
BLANK	--	15	
STD 1	46	15	
STD 2	47	15	
STD 3	48	15	
STD 4			
STD 5			
SAMPLES	--	15	

LAST SAMPLE NO. = 45 MULTIPLE INJECTIONS = 1
 NO. OF REPLICATES = 3 LAST DRY PHASE STEP = 2
 RESLOPE RATE = 6 INJECTION TEMP. =AMB
 FIRST SAMPLE NO. = 1

Ni

STEP NO.	TEMPERATURE °C.	TIME SEC.	GAS FLOW	GAS TYPE	READ COMMAND
1	75	5.0	3.0	NORMAL	
2	90	100	3.0	NORMAL	
3	120	10	3.0	NORMAL	
4	120	5.0	3.0	NORMAL	
5	1000	5	3.0	NORMAL	
6	1000	10	3.0	NORMAL	
7	1000	2.0	0	NORMAL	
8	2400	0.7	0	NORMAL	*
9	2400	2.0	0	NORMAL	*
10	2400	1.0	3.0	NORMAL	*
11	40	12	3.0	NORMAL	

SAMPLES AND STANDARDS	TYPE	VOLUME	MODIFIER
BLANK	--	50	
STD 1	46	50	
STD 2	47	50	
STD 3	48	50	
STD 4			
STD 5			
SAMPLES	--	50	

LAST SAMPLE NO. = 45 MULTIPLE INJECTIONS = 1
 NO. OF REPLICATES = 3 LAST DRY PHASE STEP = 2
 RESLOPE RATE = 5 INJECTION TEMP. =AMB
 FIRST SAMPLE NO. = 1

Co

STEP NO.	TEMPERATURE °C.	TIME SEC.	GAS FLOW	GAS TYPE	READ COMMAND
1	75	5.0	3.0	NORMAL	
2	90	50	3.0	NORMAL	
3	120	10	3.0	NORMAL	
4	120	5.0	3.0	NORMAL	
5	1000	5	3.0	NORMAL	
6	1000	10	3.0	NORMAL	
7	1000	2.0	0	NORMAL	
8	2400	0.8	0	NORMAL	*
9	2400	2.0	0	NORMAL	*
10	2400	1.0	3.0	NORMAL	*
11	40	12	3.0	NORMAL	

SAMPLES AND STANDARDS	TYPE	VOLUME	MODIFIER
BLANK	--	25	
STD 1	46	25	
STD 2	47	25	
STD 3	48	25	
STD 4			
STD 5			
SAMPLES	--	25	

LAST SAMPLE NO. = 45 MULTIPLE INJECTIONS = 1
 NO. OF REPLICATES = 3 LAST DRY PHASE STEP = 2
 RESLOPE RATE = 5 INJECTION TEMP. =AMB
 FIRST SAMPLE NO. = 1

Reagents

Hydrofluoric acid, concentrated (48-51%), (sp gr 1.17).

Nitric acid, concentrated, (sp gr 1.41).

Nitric acid, concentrated, ultrapure, (sp gr 1.41).

Perchloric acid, concentrated (70-72%), (sp gr 1.67).

Phosphoric acid, concentrated (85%), (sp gr 1.83).

Phosphoric acid, dilute (5 + 995): add 5 mL concentrated phosphoric acid (sp gr 1.83) to 800 mL demineralized water. Dilute to 1 L in a volumetric flask with demineralized water and store in a Teflon bottle. Prepare fresh for each batch of samples.

Rinse solution: add 25 mL ultrapure concentrated nitric acid (sp gr 1.41) to 400 mL demineralized water, add 50 μ L dilute Triton X-100 solution, and dilute to 500 mL in a volumetric flask. Store in a Teflon bottle. Prepare as needed.

Mixed salt standard stock solution I (minors): Dissolve the following compounds or elements: cadmium metal (0.200 g), chromium metal (0.800 g), cobalt metal (1.200 g), copper metal (0.800 g), lead metal (2.000 g), lithium carbonate (2.130 g), manganese metal (2.000 g), nickel metal (1.200 g), strontium carbonate (1.685 g), and zinc metal (0.320 g). Add 20 mL concentrated ultrapure nitric acid (sp gr 1.41), and dilute to 1,000 mL with demineralized water. This solution will contain the following concentrations:

cadmium (200 mg/L), chromium (800 mg/L), cobalt (1,200 mg/L), copper (800 mg/L), lead (2,000 mg/L), lithium (400 mg/L), manganese (2,000 mg/L), nickel (1,200 mg/L), strontium (1,000 mg/L), and zinc (320 mg/L). Store in a Teflon bottle. This solution is stable for 1 year².

Mixed salt standard solution II (minors): Take 100 mL of mixed salt standard stock solution I, add 20 mL ultrapure concentrated nitric acid (sp gr 1.41), and dilute to 1,000 mL. This solution will contain the following concentrations: cadmium (20 mg/L), chromium (80 mg/L), cobalt (120 mg/L), copper (80 mg/L), lead (200 mg/L), lithium (40 mg/L), manganese (200 mg/L), nickel (120 mg/L), strontium (100 mg/L), and zinc (32 mg/L). Store in a Teflon bottle. Solution is stable for 3 months.

Mixed salt standard stock solution III (majors): Dissolve the following compounds or elements: aluminum metal (1.500 g), calcium carbonate (1.249 g), iron metal (1.000 g), magnesium (0.200 g), manganese metal (0.040 g), potassium chloride (0.668 g), sodium chloride (0.636 g), and ammonium titanyl oxalate (1.2227 g), add 20 mL ultrapure concentrated nitric acid (sp gr 1.41), and dilute to 1,000 mL with demineralized water. This solution will contain the following concentrations: aluminum (1,500 mg/L), calcium (500 mg/L), iron (1,000 mg/L), magnesium (200 mg/L), manganese (40 mg/L), potassium (350 mg/L), sodium (250 mg/L), and titanium (200 mg/L). Store in a Teflon bottle. Solution is stable for 1 year².

²A mixed salt standard solution of this type can be obtained commercially and, provided that it is of sufficient purity, can be substituted for the prepared mixture.

Working standard solution I: Take respectively, a 10 mL (1), 5 mL (2), and 1 mL (3) aliquot of mixed salt standard solution II, add to each, 4 mL ultrapure concentrated nitric acid (sp gr 1.41), 20 mL of mixed salt standard stock solution III, and dilute to 200 mL in volumetric glassware with demineralized water. Store in Teflon bottles. Prepare fresh for each analysis.

Working standard solution II: Take respectively, 10 mL aliquots of solutions 1 (4), 2 (5), and 3 (6), add 2 mL ultrapure concentrated nitric acid (sp gr 1.41), and dilute to 100 mL in volumetric glassware with demineralized water. Store in Teflon bottles. Prepare fresh for each analysis.

Working standard solution III: Take 10 mL aliquots of solutions 4 (I), 5 (II), and 6 (III), add 2 mL ultrapure concentrated nitric acid (sp gr 1.41), and dilute to 100 mL in volumetric glassware with demineralized water. Store in Teflon bottles. Prepare fresh for each analysis. Concentrations are as follows :

Element	Standard I ($\mu\text{g/L}$)	Standard II ($\mu\text{g/L}$)	Standard III ($\mu\text{g/L}$)
Cu	40	20	4
Zn	16	8	1.6
Pb	100	50	10
Cr	40	20	4
Ni	60	30	6
Co	60	30	6

These solutions are used for all analyses except Cd.

Working standard solution IV (Cd): Take respectively, 10 mL (7), 5 mL (8), and 1 mL (9) of mixed salt solution II, add 20 mL ultrapure concentrated nitric acid (sp gr 1.41), and dilute to 1,000 mL in volumetric glassware with demineralized water. Store in Teflon bottles. Prepare fresh for each analysis.

Working standard solution V (Cd): Take respectively, 10 mL aliquots of solutions 7 (10), 8 (11), and 9 (12) from above, add 2 mL ultrapure concentrated nitric acid (sp gr 1.41), and dilute to 100 mL in volumetric glassware with demineralized water. Store in Teflon bottles. Prepare fresh for each analysis.

Working standard solution VI (Cd): Take 10 mL aliquots of solutions 10 (IV), 11 (V), and 12 (VI), add 2 mL ultrapure concentrated nitric acid (sp gr 1.41), and dilute to 100 mL in volumetric glassware with demineralized water. Store in Teflon bottles. Prepare fresh for each analysis. Concentrations are as follows:

Element	Standard I ($\mu\text{g/L}$)	Standard II ($\mu\text{g/L}$)	Standard III ($\mu\text{g/L}$)
Cd	2	1	0.2

These solutions are used for the analysis of Cd.

Triton X-100 solution

Triton X-100 solution, dilute: Take 10 mL Triton X-100 solution and add it to 800 mL demineralized water. Dilute to 1 L in volumetric glassware and store in a Teflon bottle. Prepare as needed.

PROCEDURE

Immediately before each use, clean all glassware by rinsing, first with ultrapure concentrated nitric acid (sp gr 1.41), and then 3 to 4 times with demineralized water.

Dry the sample by an appropriate procedure such as freeze-drying or in an oven at 105°C. Grind the sample with an agate mortar and pestle until all material is finer than 100 mesh.

Accurately weigh and transfer an aliquot of finely ground sample to a 100 mL Teflon beaker; weigh out corresponding standard materials as well, and use several empty beakers for blanks³.

Place the hot plate in a perchloric acid hood, turn on the hood and hot plate, and adjust the hot plate to produce a surface temperature of 200°C. To each beaker, add 6 mL concentrated nitric acid (sp gr 1.41), and place the beakers on the hot plate for approximately 30 minutes⁴.

³This procedure can be used with sample weights up to 1.000 g, with appropriate adjustments to the final solution volumes and acid strengths. The standards, calculations, and reporting limits are based upon a digested sample size of 5 mg brought up in 50 mL for a dilution factor of 10,000. Either adjust the final volume to conform to this ratio or adjust the calculations accordingly.

⁴This step is designed to oxidize organic matter in the sample. It is imperative that this step be carried out prior to the addition of perchloric acid, otherwise an explosion could occur.

Remove the beakers from the hot plate and wait 5 minutes. Add 6 mL hydrofluoric acid (sp gr 1.17) and 2 mL perchloric acid (sp gr 1.67), and return the beakers to the hot plate. Continue heating until the evolution of white perchloric fumes and the solutions have reached incipient dryness; however, do not bake the residues. Repeat this step.

Remove the beakers from the hot plate and wait 5 minutes. Add 2 mL perchloric acid (sp gr 1.67) and return the beakers to the hot plate. Continue heating until the evolution of white perchloric fumes and the solution reaches incipient dryness; however, do not bake the residue.

Remove the beakers from the hot plate, lower the hot plate temperature to 100°C, add 1 mL ultrapure concentrated nitric acid (sp gr 1.41) and swirl the beaker; add 10 mL demineralized water and return to the hot plate until the residues dissolve.

Cool the beakers, and pour each solution into an appropriate volumetric flask. Rinse the beaker several times with demineralized water and make to the mark with demineralized water. Pour the solution into a Teflon bottle for storage⁵.

⁵If the starting sample weight was 5 mg, and the final volume is 50 mL, the solution represents a dilution factor of 10,000. Also, see footnote 3.

Set up the atomic absorption spectrophotometer as shown in table 2, and program the graphite furnace and autosampler as shown in table 3. All sample cups for the autosampler should be soaked in ultrapure concentrated nitric acid (sp gr 1.41), and then rinsed 3 or 4 times with demineralized water. Before filling each sample cup, it should then be rinsed 3 or 4 times with the sample, prior to filling⁶.

Proceed to analyze the samples. Dilute samples further, if required⁷.

Calculations and Reporting Limits

Determine the concentration of each constituent in the 10,000 X solutions (Cu, Zn, Cd, Pb, Cr, Ni, and Co) from the digital display based upon the average of three separate determinations on each solution, and record the results.

The actual concentration of each constituent in the samples can be obtained by multiplying the concentration solution by 10,000 if no further dilutions are made. Likewise, if multiple injections (n times) are used, the actual concentration in the sample can be obtained by multiplying the solution concentration by $(10,000)/(n)$.

⁶It is possible to pre-clean the sample cups by soaking overnight in dilute nitric acid, washing them with demineralized water, and storing them in demineralized water. However, storage should be in sealed containers. If there is a potential for contamination, it is better to follow the procedure outlined.

⁷Experience has shown that furnace tubes must be "conditioned" prior to carrying out analyses. First, insure that the autosampler capillary is accurately placed to inject the sample through the furnace tube sample hole. Press the "Tube Clean" button 3 or 4 times. Then condition the tube by injecting 5 or 6 aliquots of the middle or high standard, with the furnace proceeding through the entire analytical program. "Conditioning" is especially critical when using a matrix modifier (in this case 0.5% H₃PO₄). Therefore, it is advisable to carry out all the "non-modifier" analyses in a group, before switching to the "modifier" analyses. Further, tube wear should be closely monitored. They generally last through 100-125 atomizations (about 30 to 40 samples, if three determinations are averaged per sample).

The reporting limits for each constituent are as follows: copper (nearest 1 mg/kg), zinc (nearest 1 mg/kg), cadmium (nearest 0.1 mg/kg to 10 mg/kg, above 10 mg/kg, nearest 1 mg/kg), lead (nearest 1 mg/kg), chromium (nearest 1 mg/kg), nickel (nearest 1 mg/kg), and cobalt (nearest 1 mg/kg).

Precision and Accuracy

The precision and accuracy of this method were determined by replicate analyses (actual separate calibrations and quantitations, but not separate digestions) of National Bureau of Standards Standard Reference Materials and on U.S. Geological Survey Rock Standards. Because most reference material certifications require a minimum 0.5 gram aliquot to obtain the stated precision and accuracy, 0.5 gram aliquots were digested following the procedures outlined above. These digestates were then serially diluted to 1/10,000. Metal quantitation was then performed on these solutions. The results are presented in table 4. The data show that the method is capable of generating both precise and accurate analytical results. The high imprecision for several of the lower concentrations (Cd in W-2, Ni in G-2) are based on single injection quantitations and would likely have been improved by a multiple injection determination.

Discussion and Results

To further evaluate the precision and accuracy of this method, 6 natural freshwater sediment samples were dried, digested, and analyzed. The samples came from different geological settings and water bodies (Appalachicola River, Fla.; Patuxent River, Md.; Doane Lake Outlet, Oreg.; Mississippi River, La.; Ned Wilson Lake, Colo.; Yaharra River, Wis.). As with the standard reference materials, 0.5 gram aliquots were digested and serially diluted to 1/10,000. These samples had been analyzed previously by both flame and flameless techniques in two different laboratories (Horowitz and Elrick, 1985), and the results are presented in table 5. As shown by the comparative data on standards and samples, analytical precision and accuracy, is quite good (tables 4 and 5). All these results indicate that precise and accurate analyses can be obtained on rocks and sediments, with as little as a 5 mg sample, by graphite furnace atomic absorption spectroscopy.

Table 5.--Comparison of results (in mg/kg)

[Includes procedures for selected sediment samples]

Sample	Method	Cu	Zn	Cd	Pb	Cr	Ni	Co
Appalachicola River, R. M. 94	a ¹	4	23	<0.5	12	23	4	10
	b ²	6	23	.03	15	20	6	10
	c ³	5	22	<.15	15	22	7	12
Patuxent River, at Hog Point	a	20	111	0.8	22	56	26	32
	b	20	110	.5	25	59	27	33
	c	19	112	.5	22	57	26	34
Doane Lake Outlet	a	33	127	<0.5	29	58	34	25
	b	35	130	.14	32	56	29	28
	c	32	127	<.15	33	54	33	28
Mississippi River at Venice	a	28	120	0.9	32	76	37	16
	b	30	120	.5	32	77	36	16
	c	26	125	.5	31	72	39	15
Ned Wilson Lake	a	28	113	0.9	38	90	66	20
	b	30	110	.4	37	90	55	20
	c	28	115	.3	37	90	65	20
Yaharra River	a	13	28	<0.5	23	28	11	18
	b	12	27	.1	22	30	13	16
	c	10	29	<.15	21	28	18	15

a¹ - Flame AAS quantitation after 0.5 g digestion with HF/HClO₄/HNO₃ (Horowitz and Elrick, 1985a, b).

b² - U.S. Geological Survey, Branch of Analytical Services, Reston, Va., determined on a sample digested with HF/HClO₄/HNO₃.

Cu - digestate extracted with butyl acetate, further extracted with diethyldithiocarbamate in chloroform, dried, brought up in HCl, graphite furnace.

Zn - see Cu, quantitation by flame AAS.

Cd - see Cu.

Pb - see Cu.

Cr - digestate diluted 1:10, quantitation by graphite furnace.

Ni - see Cr.

Co - See Cr.

c³ - This method.

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